

Fig. 3 shows the changes, as the fractionation proceeded, in the intensities of certain specified bands of those earths that yield absorption spectra.

Examination of these curves shows that with an original material of an atomic weight of 116 containing earths of the yttrium, erbium and didymium groups fractional crystallization of the picrates from aqueous solution yields the following results:

(1) A concentration of praseodymium and neodymium in the first fractions followed by rapid decrease of these two elements after the sixth fraction.

(2) A peculiar increase in the amounts of praseodymium and neodymium in the tenth and nineteenth fractions.

(3) A sudden concentration of erbium and holmium in the eighth fraction, and an entire absence of these two elements in the first six fractions of the series. To ascertain whether there was any detectable amount of erbium in the sixth fraction, the 20% solution of the chlorides used for the examination of the absorption spectrum was evaporated to a thick syrup and its spectrum reexamined. Even under this conditions no erbium bands were visible.

The fractional crystallization of the picrates of the rare earths appears to furnish excellent means of effecting a rapid concentration of praseodymium and neodymium practically free from erbium and holmium, and concentration of erbium and holmium with but relatively small amount of the members of the didymium group. The peculiar rise in the concentration of praseodymium and neodymium in the tenth and nineteenth fractions is under further investigation.

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THE SOLUBILITY OF IODINE IN AQUEOUS SOLUTIONS OF BROMIDES OF POTASSIUM AND SODIUM.

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The great increase in the solubility of iodine in water due to the presence of iodides and of bromine due to the presence of bromides has been attributed to the formation in solution of polyiodides and polybromides.¹ Some of these polyhalides have been isolated. The compound KI_3 has been described by Johnson,² but its existence at 25° has been questioned by Abegg and Hamburger;³ this same compound has been described also by Wells, Wheeler and Penfield,⁴ who have also recorded the follow-

¹ This same phenomenon has been called by Parsons, "Solution in a dissolved solid" (*J. Physic. Chem.*, 11, 659 (1907)).

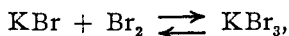
² *J. Chem. Soc.*, 31, 247 (1877).

³ *Z. anorg. Chem.*, 50, 403 (1906).

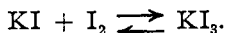
⁴ Wells and Penfield, *Am. J. Sci.*, [3] 43, 17 (1892); Wells, Wheeler and Penfield, *Ibid.*, [3] 43, 475 (1892); 44, 42 (1892).

ing compounds of the same type together with analyses, crystallographic data and methods of formation: CsI_3 , CsBr_3 , RbI_3 , RbBr_3 ; and also the higher polyhalides: CsI_5 and CsBr_5 . Still higher bromides and iodides have been isolated. Abegg and Hamburger¹ obtained KI_7 from benzene solutions containing potassium iodide and iodine.

Besides the above direct evidence of the existence of polyhalides, certain physical properties of solutions containing a salt of a halogen and the free halogen indicate that some union of these has taken place. LeBlanc and Noyes² found that the freezing point of a normal solution of potassium iodide was slightly raised by the addition of iodine to the solution, and the conductance of this salt solution was diminished by the presence of pure iodine. In a recent paper by Joseph and Jinendradasa³ it is shown that bromides lighten the color of aqueous bromine solutions, the diminution of color depending on the amount of bromide added. Making the assumption that the principal action causing the color change is the formation of a tribromide,



and applying the law of mass-action to this reversible reaction, these authors obtained a satisfactory constant. In all probability, therefore, the correct assumption was made as to the nature of the reaction. Jakovkin⁴ had previously made the same assumption in the case of the iodides, namely, that the reaction may be expressed thus:



Here the quantity of uncombined iodine was determined by distribution experiments, the liquids being carbon disulfide and water in which the iodide was dissolved. The results of Dawson and Goodson⁵ indicate that iodine and sodium iodide unite when dissolved in nitrobenzene; for, the solution saturated with respect to both contains over ten times as much iodine as the solution saturated with iodine alone, and over ten times as much sodium iodide as the solution saturated with sodium iodide alone.

Thus, there are both direct and indirect evidences that some sort of union takes place between a halogen and its salt in aqueous solution.

There have also been recorded by Wells, Wheeler and Penfield⁶ the following compounds between a halogen and the salt of another halogen: CsBrI_2 , CsBr_2I , CsClBrI , CsCl_2I , CsClBr_2 , CsCl_2Br , RbBr_2I , RbClBrI ,

¹ *Loc. cit.*

² *Z. physik. Chem.*, 6, 401 (1890).

³ *J. Chem. Soc.*, 99, 274 (1911).

⁴ *Z. physik. Chem.*, 13, 539 (1894).

⁵ *J. Chem. Soc.*, 85, 794 (1904).

⁶ Wells and Penfield, *Amer. J. Sci.*, [3] 43, 17 (1892); Wells, Wheeler and Penfield, *Ibid.*, 43, 475 (1892); 44, 42 (1892).

RbCl₂I, RbClBr₂, RbCl₂Br, KBr₂I, KCl₂I, CsCl₄I, RbCl₄I, KCl₄I, NaCl₄I.2H₂O, LiCl₄I.4H₂O. With this direct evidence that mixed salts are also formed, it might be expected that there would also be the indirect evidence of a great increase in solubility of a halogen due to the presence in solution of a salt of another halogen; for example, that the solubility of iodine would be very greatly increased by the presence of an alkali bromide, just as the presence of one mole of potassium bromide in dilute solution causes one mole of bromine to pass into solution, and more than one mole of bromine when the solution is more concentrated.¹ Furthermore, the work of Dawson and Goodson,² using nitrobenzene as solvent and potassium bromide and iodine as solutes, seems to indicate some union of the solutes. Both of these solutes alone have relatively slight solubilities in nitrobenzene, but each influences the solubility of the other in a very remarkable way. The solution saturated with both potassium bromide and iodine contains 2.52 moles I₂ and 0.71 moles potassium bromide per liter. Regarding the possibility of the formation of compounds, the authors say: "The two series of solutions approximate in composition as the concentration increases, and the identity of the two final solutions indicates that saturation with regard to both components has now been reached. The composition of the solution saturated with iodine makes it appear probable that the complex perhalogen compounds present in solution are of the same type as those in solutions of the alkali iodides, although the evidence in support of this view is not nearly so decisive."

The present work was undertaken to determine whether double compounds of iodine with sodium or potassium bromide were indicated by a possible large increase in solubility of the halogen due to the presence of the bromide in aqueous solution. The method of procedure was similar to that of Worley,³ who determined the quantity of bromine dissolved in various potassium bromide solutions.

To aqueous solutions of sodium and potassium bromides, iodine was added in excess, and the bottles were rotated in a thermostat at 25°, electrically heated and controlled. Equilibrium was shown to be established when titrations for free iodine gave the same results as on one or two days previously. The following table and figure give these results.

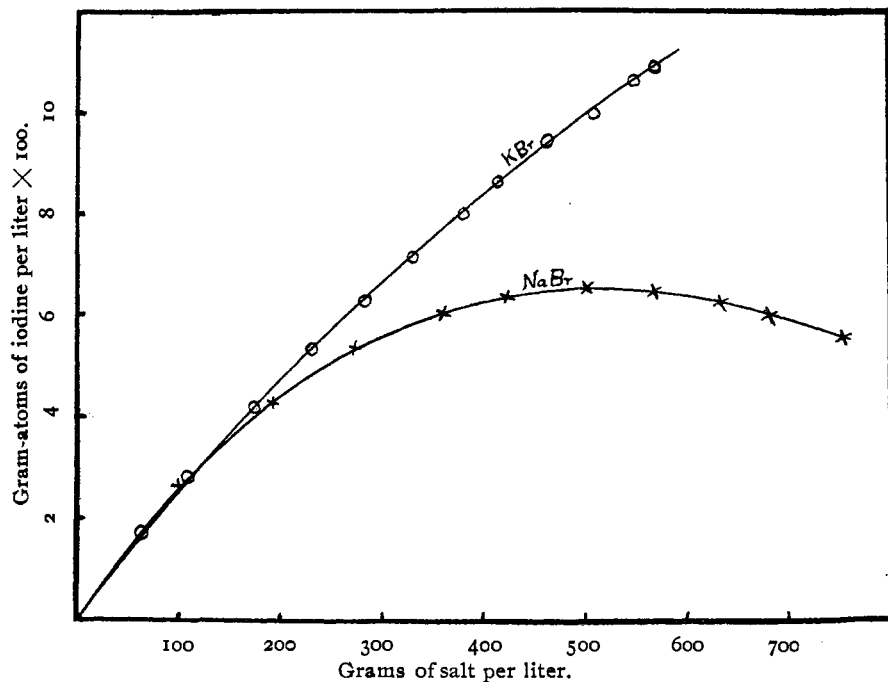
Each curve is concave downwards, indicating that each successive addition of the salt causes the solubility of iodine to increase by smaller and smaller amounts. These curves are unlike the curve of Worley³ for the solubility of bromine in potassium bromide solutions, where

¹ Worley, *J. Chem. Soc.*, 87, 1107 (1905).

² *J. Chem. Soc.*, 85, 796 (1904).

³ *Loc. cit.*

NaBr per liter Grams.	Iodine per liter. Gram-atoms.	KBr per liter. Grams.	Iodine per liter. Gram-atoms.
96.4	0.0266	60.6	0.0176
187.7	0.0425	106.9	0.0278
271.8	0.0538	175.9	0.0415
357.4	0.0598	229.8	0.0532
422.4	0.0638	281.9	0.0628
499.1	0.0648	330.6	0.0717
569.9	0.0644	377.1	0.0797
632.0	0.0622	411.0	0.0864
679.7	0.0595	461.7	0.0948
750.5	0.0551	509.8	0.1006
756.1 (sat'd)	0.0550	548.0	0.1062
		567.9 (sat'd)	0.1094



each successive addition of the salt causes the solubility of bromine to increase by greater and greater amounts. Not only are these cases different from that of Worley in kind but also in degree. For each mole of bromide in solution there was at least one mole of bromine in excess of that dissolved by the water alone. In the present cases the increase in solubility of iodine is of the order 10^{-2} mole iodine for each mole of salt. Moreover, in concentrated solutions of potassium bromide the ratio is somewhat less than 10^{-2} and in concentrated solutions of sodium bromide the ratio is considerably less than 10^{-2} . Consequently it follows from these solu-

bility measurements, that if compounds of iodine and a bromide exist at all in aqueous solution, they are present in very minute quantities.

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THE SOLUBILITY OF BROMINE IN AQUEOUS SOLUTIONS OF SODIUM BROMIDE.

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Reference was made in the preceding paper to the results of Worley on the solubility of bromine in solutions of potassium bromide and of Joseph and Jinendradasa on the color changes in bromine solutions due to the addition of bromides. The following table and figure give the results of solubility determinations of bromine in solutions of sodium bromide at 25°. The free bromine was estimated by adding a known volume of the solution to an excess of an iodide solution. The iodine liberated was

NaBr per liter. Grams.	Bromine per liter. Gram-atoms.	Density.
92.6	2.479	1.213
160.5	4.345	1.372
205.8	6.195	1.515
255.8	8.575	1.678
319.7	13.65	1.997
359.0	16.04	2.137
...	19.23	2.327
408.3	20.85	2.420

